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GLASS CERAMICS BASED ON OIL SHALE ASH

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The experience of synthesizing glass ceramics of pyroxene composition based on the mineral component formed by pyrogassing of solid types of fuel, in particular, in processing oil shale is generalized. The structure and properties of glass ceramics produced by various molding methods are studied.

Combustible shale is widely used as a fuel for steam and electric power plants in Russia, Estonia, Latvia, Germany, Poland, and China. Accordingly, the problem of utilization of ash generated by these power plants is topical. In our previous studies [1 – 3], we demonstrated the possibility of producing pyroxene glass ceramic based on this waste. However, the effect of molding methods on the structure and properties of such glass ceramics has not been studied. This issue is the object of the present investigation.

The main component for glass melting was ash of oil shale from the Perelyub-Blagodatskoe deposit (Saratov Region) of the following composition (here and elsewhere wt.%): 40.7 SiO₂, 12.5 Al₂O₃, 2.1 FeO, 6.7 Fe₂O₃, 22.7 CaO, 1.5 MgO, 0.7 TiO₂, 0.8 P₂O₅, 0.5 Na₂O, 2.8 K₂O, 6.7 SO₃, and 2.3 H₂O. The additives (above 100% ash) were charcoal (1%) and Cr₂O₃ (0.3%). The resulting batch was used to melt glass in alundum crucibles for 80 min at 1380°C under laboratory conditions. The obtained glass melt was homogeneous and free of glass-melting defects. The chemical composition of the glass was as follows (%): 42.3 SiO₂, 14.9 Al₂O₃, 1.9 FeO, 10.9 Fe₂O₃, 19.9 CaO, 2.0 MgO, 0.8 TiO₂, 0.9 P₂O₅, 1.8 Na₂O, 4.0 K₂O, 0.4 SO₃, and 0.2 Cr₂O₃. According to the data of the previous studies [3], the optimum crystallization conditions for such glass include consecutive heat treatment at 750 and 950°C. The glass melt was used for the production of glass ceramics using various methods.

Casting and subsequent crystallization. The melt was chilled to a temperature of 1200°C and cast into a graphite mold. Next, the samples were placed into a muffle furnace and exposed for 2 h at a temperature of 750°C, then heated for 1 h up to 950°C and exposed for 2 h at this temperature. The crystallized samples were cooled for 6 h at room temperature.

Slip casting. The glass melt was poured into water. The resulting frit was milled in a ball mill. The fraction with a specific surface area of 4600 cm²/g (determined on an

LKhM 8MD chromatograph using the BET method) was used to prepare a mixture that contained (%): 86.4 glass powder, 13.6 paraffin, and 0.2 stearic acid. The mixture was prepared with a VA-282 propeller mixer at 80°C for 1 h. Samples were molded on a thermoplastic-molding machine in stainless steel molds. The molded samples were placed in an alumina charge and heated in an electric muffle furnace under the following temperature conditions: heating to 180°C (1 h), exposure at 180°C (3 h), heating to 300°C (13 h), heating to 650°C (3.5 h), exposure at 650°C (3 h), heating to 750°C (3 h), exposure at 750°C (2 h), heating to 950°C (1 h), exposure at 950°C (2 h), and cooling to room temperature (6 h).

Semidry molding. The glass powder obtained by the same method was used to prepare a work mixture (%): 92.9 glass powder, 7.0 paraffin, and 0.1 stearic acid. The work mixture was compressed for 1 min in a metal mold under a pressure of 90 MPa. The molded samples were heat-treated according to the following conditions: heating to 750°C (3 h), exposure at 750°C (2 h), heating to 950°C (1 h), exposure at 950°C (2 h), and cooling to room temperature (6 h).

The microhardness of glass ceramics was determined by the Vickers method on a PMT-3 set, the bending strength was

TABLE 1

Parameter	Molding method		
	casting with subsequent crystallization	slip casting	semidry molding
Density, kg/m ³	3040	2250	2520
Microhardness, GPa	7.10	5.75	5.93
Mean mechanical strength, MPa	119	53	62
TCLE, 10 ⁻⁷ K ⁻¹	95	92	93
Acid resistance, %	98.5	96.4	97.1
Alkali resistance, %	88.0	85.1	86.2
Water resistance, %	99.9	98.9	99.2

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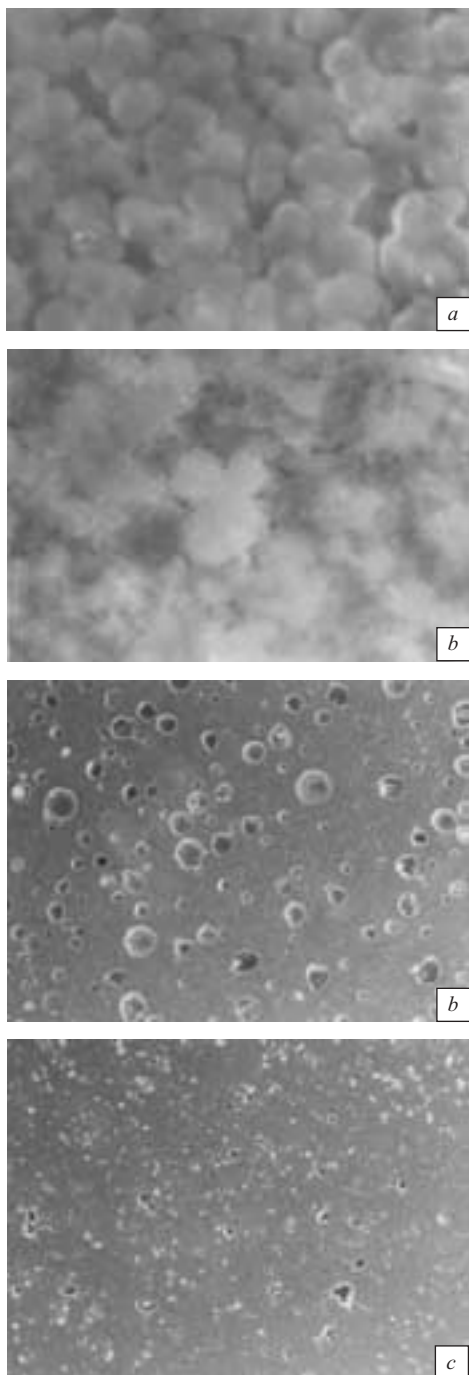


Fig. 1. Electron microscope photos of the structure of glass ceramics produced by casting with subsequent crystallization (*a*), slip casting (*b*), and semidry molding (*c*).

measured on an EP-5046-5 breaking machine, the chemical resistance determined by the powder method (GOST 10134–82), and the TCLE was measured on a Harrop TDA-H1-APG-SC dilatometer.

The structure and the chemical composition of the materials were studied using electron scanning microscopy and local microanalysis (a Jeol-5800LV electron microscope

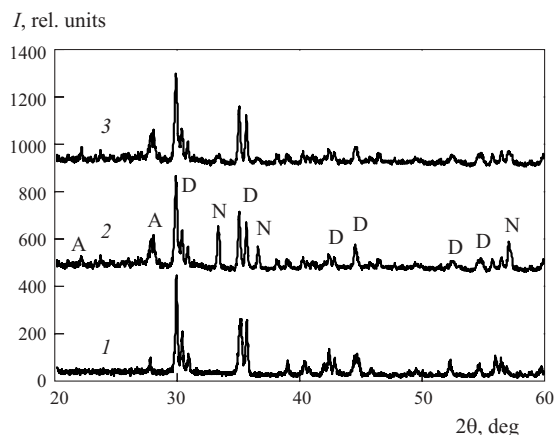


Fig. 2. Diffraction patterns of glass ceramics based on oil shale ash produced by casting with subsequent crystallization (*1*), slip casting (*2*), and semidry molding (*3*): D) diopside; A) albite, N) andradite.

equipped with an EDS-S60 DX90 x-ray microanalyzer) and x-ray phase analysis (a Philips X'Pert-MPD diffractometer).

The chemical composition and the properties of the glass ceramics are given in Table 1, and the electron microscope photos of their structure and the diffraction patterns are shown in Figs. 1 and 2, respectively.

The different methods of molding glass ceramics, despite using glass of identical chemical composition and the same heat-treatment conditions in the temperature range 750–950°C, have certain specifics, which are manifested in the different phase compositions and structures of the materials obtained.

First of all, we should note a difference between the processes of the surface and volume crystallization. The large geometrical surface of the glass powder used in slip casting and semidry molding increases the effect of the surface crystallization processes. A comparison of the phase composition of glass ceramics obtained by different methods from glass of the same composition indicated that in using the powder methods, the content of the main crystalline (pyroxene) phase is higher in slip casting and semidry molding. At the same time, the content of additional crystalline phases (wollastonite, andradite) increases, presumably under the effect of the surface crystallization. One should also note the difference in the microstructure of samples produced by the powder methods and by casting (Fig. 1). In the first case, the size of the crystals is smaller, and in the second case the crystal boundaries are more blurred due to the presence of fine-crystalline phases.

Another distinction in the crystallization conditions is related to the reducing medium created inside the muffle furnace due to the volatilization and oxidation (burning out) of the hydrocarbonates contained in the slip. It is known that the chemical composition of the atmosphere has an effect on the surface crystallization processes in silicate glasses [4]. Since the quantity of the hydrocarbon binder used in slip casting

and semidry molding differs, a comparison of the data on the structure and properties of glass ceramics produced by these methods makes it possible to estimate the effect of the products of oxidizing pyrolysis of paraffin on the crystallization processes.

A comparison of the diffraction patterns of the samples produced by casting and semidry molding indicates that in spite of the predominance of the pyroxene crystalline phase (diopside) in both materials, the content of albite $\text{NaSi}_3\text{AlO}_8$ and andradite $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ is significantly higher in the samples based on glass powders. Since these crystalline phases are virtually absent in the samples produced by glass melt casting, it is obvious that their formation is facilitated by surface crystallization, whose effect is significantly more perceptible in the powder technologies. On the other hand, the creation of more clearly expressed reducing conditions in the atmosphere increases the rate of andradide formation.

Thus, the main pyroxene phase in the form of diopside and diopside-hedenbergite solid solutions is formed regardless of the surface crystallization. However, the higher specific surface area of the samples produced by the powder methods and subsequent thermal treatment facilitates an increased content of albite and andradide crystals in the glass ceramic structure. At the same time, andradide is mainly formed under surface crystallization in reducing conditions.

The use of powder methods and an organic binder in molding is related to the formation of a porous structure in

glass ceramics. The porosity of the samples produced by slip casting (with a higher content of organic binder) is higher than that of the samples produced by semidry molding, which leads to a decreased mechanical strength. An additional effect is produced by a higher molding pressure in semidry molding, which provides for a denser packing of the glass powder particles.

Thus, the method of molding of pyroxene glass ceramics has an effect on their phase composition, structure, and properties, and therefore, ought to be taken into account in determining the application area of glass ceramics.

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